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Ullmann's Encyclopedia of Industrial Chemistry

Sixth, Completely Revised Edition

Volume 6

Butenes
to
Cellulose Ethers

WILEY-VCH

unit and the pyranose ring oxygen in the adjacent glucose unit of the same chain molecule. This intramolecular secondary valence bond is also responsible for the relative rigidity of the cellulose molecule [26]. Some authors [27] suggest a second intramolecular hydrogen bond involving the hydroxyl groups on C–6 and C–2 of adjacent glucose units in the same molecule.

In more recent years, some researchers suggested a unit cell for cellulose I in which the a and c axis of the Meyer–Mark–Misch model are doubled [28], [29]. However, these newer interpretations of X-ray and electron diffraction results are more or less closely related to the Meyer–Mark–Misch lattice structure. In reference [30], it is claimed that there is a closer agreement with the observed diffraction intensity data for parallel arrangement of the cellulose molecules in the unit cell. However, this is still controversial [31].

The internal cohesion of the cellulose molecules in the unit cells and crystalline domains is due to intermolecular secondary valences – partly hydrogen bonds and partly van der Waal's forces. These bonds can act either between molecules situated in the same crystal lattice plane (intraplanar bonds) or between molecules located in neighboring lattice planes (interplanar bonds). The intraplanar hydrogen bonds are formed primarily between adjacent cellulose molecules in the same 002 lattice planes giving a sheetlike structure. The 002 sheets are then bonded to one another by hydrogen bridges involving the hydroxyl groups on C–6 and the glucosidic ring oxygen atoms of cellulose molecules favorably located in neighboring 002 planes, or by van der Waal's forces acting between neighboring glucopyranose rings.

The unit cells of the other polymorphic structures of cellulose – the most important one being the so-called cellulose II – differ basically in the lengths of their a and c axis and the angle of inclination β. The cellulose II modification is formed as the thermodynamically most stable polymorph when cellulose fibers are treated with concentrated sodium hydroxide solution (> 14 %) or precipitated (regenerated) from solution.

In addition to the cellulose I and cellulose II modifications, two other polymorphic lattice structure are known, the cellulose III and cellulose IV crystal modifications. The cellulose III structure is formed when the reaction product of native cellulose fibers is decomposed with liquid ammonia. This modification has a lattice structure closely related to that of cellulose II. The cellulose IV modification is obtained by treating regenerated cellulose fibers in hot baths under stretch. The lattice of this polymorph is closely related to that of cellulose I. Some distinct differences in their infrared absorption spectra seem to indicate their existence. Some researchers however doubt their actual existence [32].

Table 3 lists the lattice parameters of the unit cells of these four polymorphic crystal structures.

Crystallites. The ability of hydroxyl groups to form secondary valence hydrogen bonds is – together with the stiff and straight chain nature of the cellulose molecule – the cause for the high tendency to organize into crystallites in parallel arrangement and crystallite strands (elementary fibrils), the basic elements of the supermolecular structure of cellulose fibers.

The dimensions of the elementary crystallites differ only slightly for native or regenerated cellulose fibers. Their length ranges between 12 and 20 nm (= 24 – 40 glucose units) and their width between 2.5 and 4.0 nm. The often observed larger "micro- or macrofibrils" (or fragments thereof) are aggregations of elementary fibrils.

Two questions concerning the crystal structure are still under dispute. The first deals with the antiparallel or parallel arrangement of the cellulose molecules in the crystal lattice as previously mentioned. The second question (still open) concerns the existence or nonexistence of folded chains in the lattice [33–35]. While a folded cellulose chain position in the lattice seems unlikely to most experts, the parallel molecule arrangement in the cellulose I lattice is principally acceptable, under the condition that two cellulose II lattice structures exist, one for heterogeneously mercerized native celluloses with parallel arrangement of the molecules and the other for regenerated cellulose substrates with antiparallel molecule arrangement.

1.1.2. Supermolecular Structure (Texture)

The basic structural element of cellulose fibers is the so-called elementary fibril. It can be seen

Table 3. Lattice p

Type	
Cellulose I	
Cellulose II	
Cellulose III	
Cellulose IV	

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Table 3. Lattice parameters of the unit cells of the cellulose polymorphs

Type	Source	Dimensions, nm			
		a	b	c	β, degree
Cellulose I	cotton	0.821	1.030	0.790	83.3
Cellulose II	cotton, mercerized	0.802	1.036	0.903	62.8
	viscose fiber	0.801	1.036	0.904	62.9
Cellulose III		0.774	1.030	0.990	58.0
Cellulose IV		0.812	1.030	0.799	90.0

with the electron microscope, as illustrated in Figure 3.

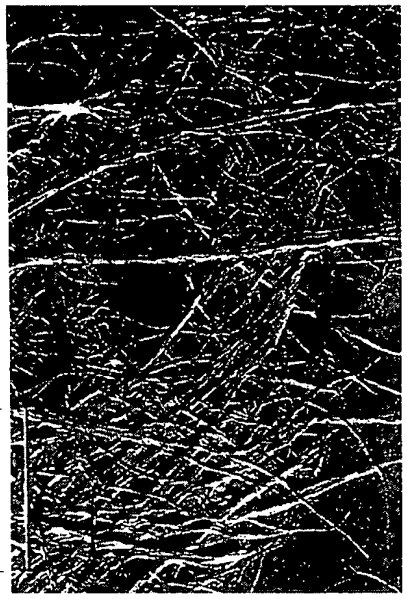

Figure 3. Electron micrograph of the fibrillar nature of cellulose fibers

The cross-dimensions of the elementary fibrils correspond with those of the elementary crystallites. The elementary fibril is a strand of elementary crystals linked together by segments of long cellulose molecules. The lateral order in the interlinking regions is distinctly less pronounced (amorphous). This structure is schematically shown in Figure 4 [36–39].

Several elementary fibrils associate to form larger aggregations of so-called microfibrils and macrofibrils, which can also be seen with a light microscope.

The elementary fibrils and their aggregations are determined by nature in such native fibers as cotton or wood pulp fibers and are laid down in various cell wall layers in a typical manner [18], [19]. Figure 5 shows the structural organisation of wood pulp and cotton fibers.

Synthetic cellulose fibers, such as viscose, do not have a native morphology. Their supermolecular structure can be described as a network of elementary fibrils and their more or less random associations. This is called a "fringe fibrillar" structure [40], which is shown in Figure 6.

Structure Characterization. The methods used to characterize the molecular and fine structure of native and synthetic cellulose fibers include the following [41]:

1) determination of the average degree of polymerization ($\bar{P}_n$) by the osmotic method;
2) determination of the average crystallite length by meridional X-ray low-angle scattering on slightly hydrolyzed fiber samples or by measurement of the band width of the meridional 040 X-ray wide-angle reflection at half-maximum intensity;
3) determination of the degree of order ("crystallinity," CrI) with a method for separating overlapping equatorial X-ray diffractions [42] and deriving from the band width at half-maximum intensity the average cross-dimensions of the crystalline regions; furthermore, this analysis yields information on the lattice structure, polymorphic composition, and accessibility;
4) determination of the degree of orientation by measuring the azimuthal intensity distribution of major equatorial X-ray diffraction arcs or by IR dichroism.

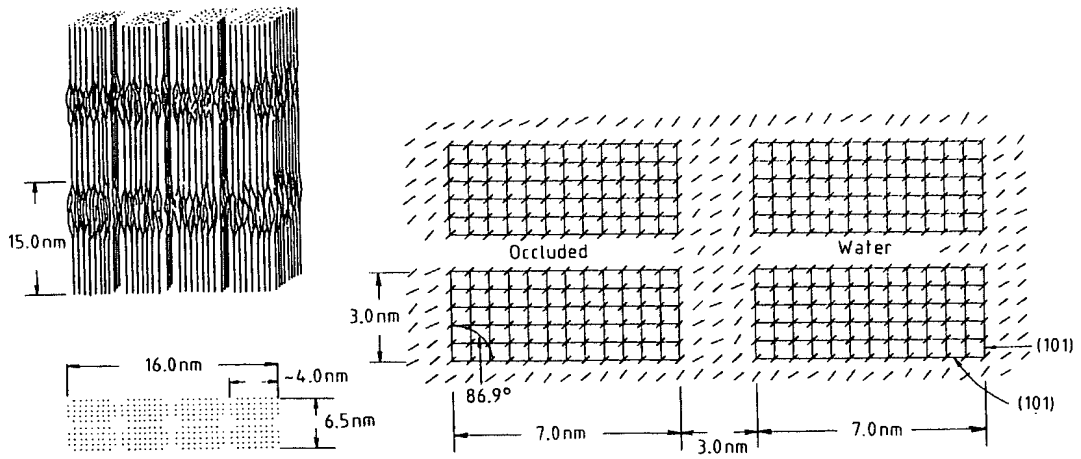

Figure 4. The architecture of elementary fibrils and microfibrils of native celluloses

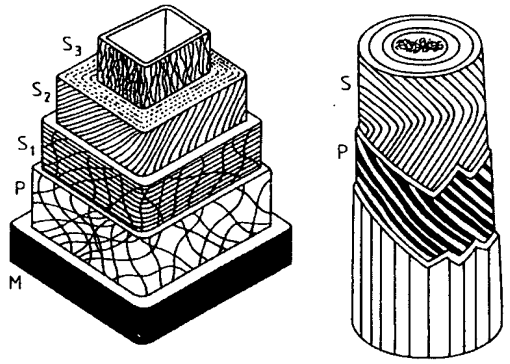

Figure 5. Positioning of the cellulose fibrils in wood (left) and cotton fibers (right)
Wood fibers: M) Middle lamella (lignin and hemicelluloses); P) Primary wall (fibril position unarranged); S_1) Secondary wall I (two or more fibrillar layers crossing one another and positioned spirally along the fiber axis); S_2) Secondary wall II (fibrils wound spirally around the fiber axis); S_3) Secondary wall III (fibrils tightly interlaced)
Cotton fibers: P) Primary wall (interlaced fibrils); S) Secondary wall (fibrils wound spirally around the fiber axis; in distinct distances along the fiber axis the spiral reverses direction)

Structure and Properties. Physicomechanical properties of cellulose fibers such as tenacities, elongations, or moduli in the conditioned or wet state are determined by the following structural parameters [43]: 1) the average length of the fiber-forming molecules ($\bar{P}_n$); 2) the average length of the elementary crystallites ($\bar{P}_{nL}$ = number average "limiting" degree of polymerization); 3) the degree of lateral order (crystallinity, CrI); 4) the degree of orientation (f_r) with respect to the fiber axis; and 5) the presence of heterogeneities (natural defects, incorporated gel or sand particles, etc.).

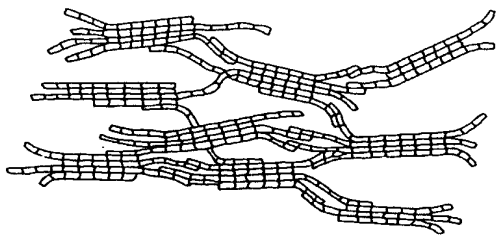

Figure 6. Fringe fibrillar model of fiber structure

This may be illustrated by the following examples: As shown by Figure 7, the tenacity of the conditioned fibers is determined by the length of the molecules in relation to the length of the elementary crystallites building the elementary fibrils ($1/\bar{P}_{nL} - 1/\bar{P}_n$), by the degree of order (CrI), and by the degree of orientation (f_r).

The elongation at break in the conditioned state is mainly dependent on the degree of orientation. Simple geometric considerations give the parameter ($1/\cos\alpha - 1$) in which the angle α derived from the orientation factor (f_r) is the mean angle of deviation of the basic structure elements from the fiber axis. Figure 8 illustrates the rela-

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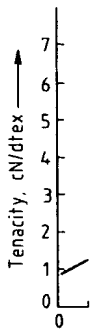

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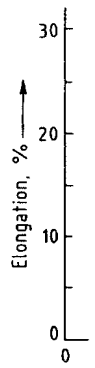

Figure 8.
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